

Claims

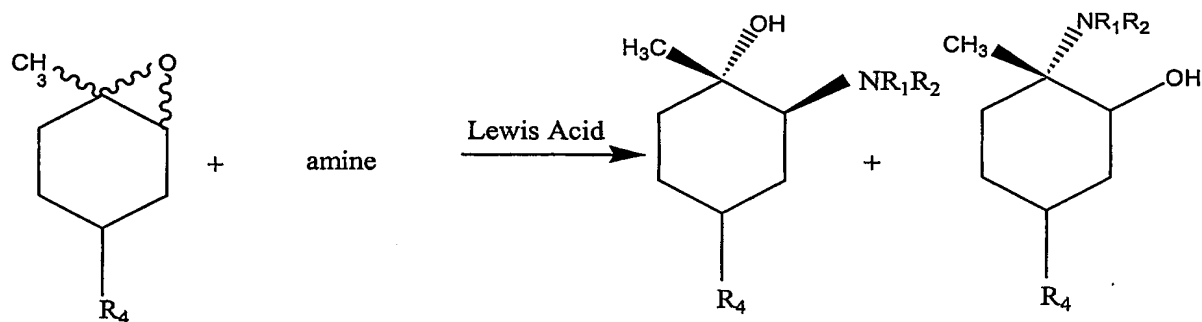
1. A process for the regio- and stereoselective opening of an epoxide ring

comprising:

reacting a compound having the epoxide ring with at least one amine in the presence of at least one Lewis acid.

2. The process according to claim 1 wherein the at least one Lewis acid is selected from the group consisting of alkyl metal halides and metal alkyl ethers.

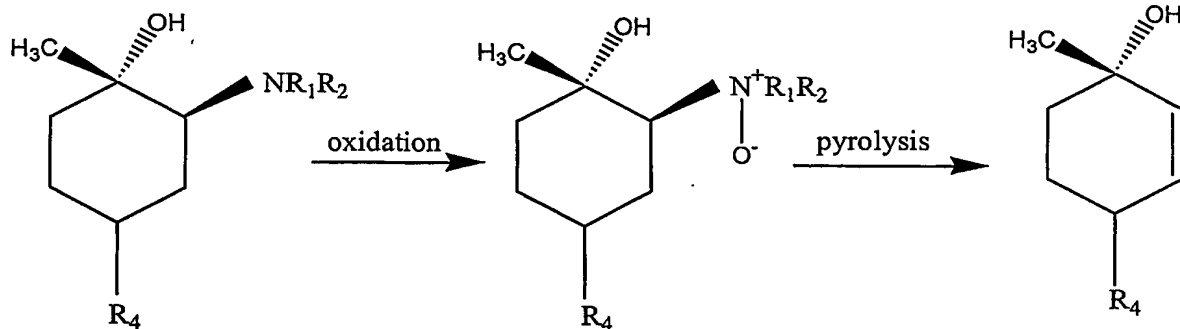
3. A process for preparing a (+)-p-mentha-2,8-diene-1-ol analog, the process comprising:



Formula (1a)

Formula (2a)

Formula (3a)



Formula (2a)

Formula (4a)

Formula (5a)

wherein R_1 and R_2 are H, alkyl or aryl;

wherein R_4 is an alkyl, alkenyl or alcohol;

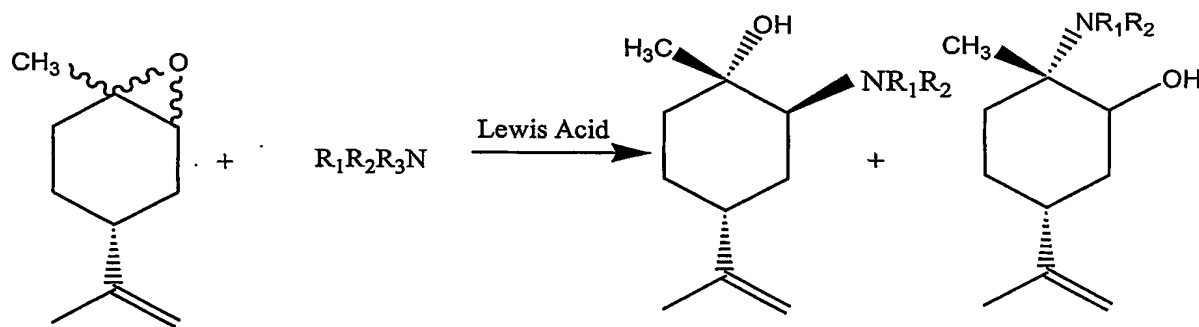
wherein step (a) comprises reacting a (+)-limonene oxide analog having the Formula (1a) with at least one amine of the formula $R_1R_2R_3N$ in the presence of at least one Lewis acid to form amine adducts having the Formula (2a) and Formula (3a);

wherein step (b) comprises oxidizing the amine adduct of Formula (2a) to form an N-oxide having Formula (4a); and

wherein step (c) comprises pyrolyzing the N-oxide of Formula (4a) to form a (+)-p-mentha-2,8-diene-1-ol analog of Formula (5a).

4. The process according to claim 3 wherein the at least one Lewis acid is selected from the group consisting of alkyl metal halides and metal alkyl ethers.

5. A process for preparing (+)-p-mentha-2,8-diene-1-ol, the process comprising:

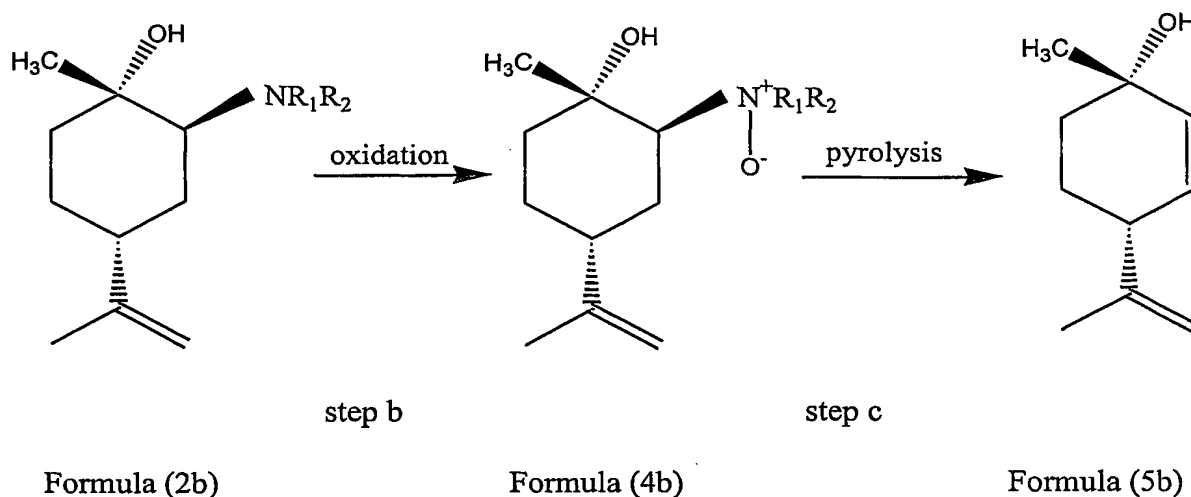


step a

Formula (1b)

Formula (2b)

Formula (3b)



wherein R₁, R₂ and R₃ are H, alkyl or aryl groups;

wherein step (a) comprises reacting (+)-limonene oxide having the Formula (1b) with at least one amine of the formula R₁R₂R₃N in the presence of at least one Lewis acid to form amine adducts having the Formula (2b) and Formula (3b);

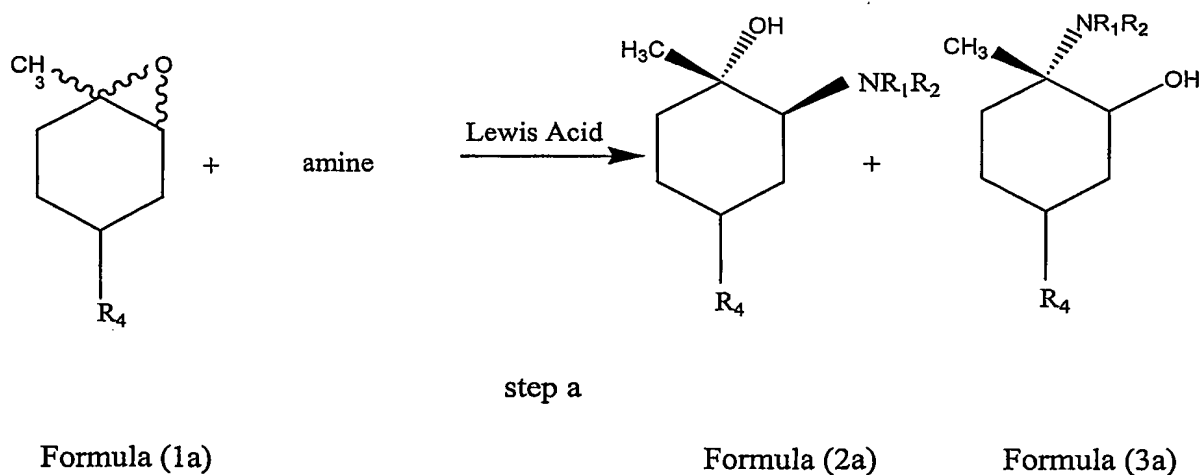
wherein step (b) comprises oxidizing the amine adduct of Formula (2b) to form an N-oxide having Formula (4b); and

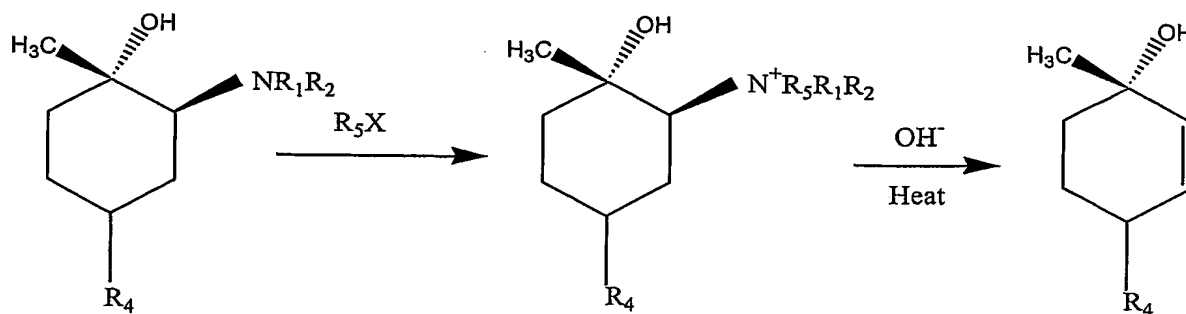
wherein step (c) comprises pyrolyzing the N-oxide of Formula (4b) to form the (+)-p-mentha-2,8-diene-1-ol of Formula (5b).

6. The process according to claim 5 wherein the at least one amine is selected from the group consisting of primary amines wherein R₁ is an alkyl or aryl group and R₂ and R₃ are H; secondary amines wherein R₁ and R₂ are alkyl or aryl groups and R₃ is H; and tertiary amines wherein R₁, R₂ and R₃ are alkyl or aryl groups.

7. The process according to claim 5 wherein the at least one Lewis acid is selected from the group consisting of alkyl metal halides and metal alkyl ethers.

8. The process according to claim 5 wherein the at least one Lewis acid includes at least one ether having the formula MOR wherein M is a metal and R is an alkyl.
9. The process according to claim 5 comprising oxidizing the amine adduct of Formula (2b) by reacting the amine adduct of Formula (2b) with at least one peracid to form the N-oxide of Formula (4b).
10. The process according to claim 5 comprising oxidizing the amine adduct of Formula (2b) by reacting the amine adduct of Formula (2b) with hydrogen peroxide in at least one alcohol to form the N-oxide of Formula (4b).
11. The process according to claim 5 comprising pyrolyzing the N-oxide of Formula (4b) in a solvent system including toluene in the presence of an at least one particulate matter selected from the group consisting of zeolites and silica gels.
12. The process according to claim 5 further including recovering the amine adduct of Formula (2b) by converting the amine adduct to an acid salt of the amine adduct of Formula (2b) by reaction with concentrated acid.
13. A process for preparing a (+)-p-mentha-2,8-diene-1-ol analog, the process comprising:





Formula (2a)

Formula (6a)

Formula (5a)

wherein R_1 , R_2 and R_3 are H, alkyl or aryl groups;

wherein R_4 is an alkyl, alkenyl or alcohol;

wherein R_5 is an H, alkyl or aryl;

wherein X is a halide;

wherein step (a) comprises reacting a (+)-limonene oxide analog having the Formula (1a) with at least one amine of the formula $R_1R_2R_3N$ in the presence of at least one Lewis acid to form amine adducts having the Formula (2a) and Formula (3a);

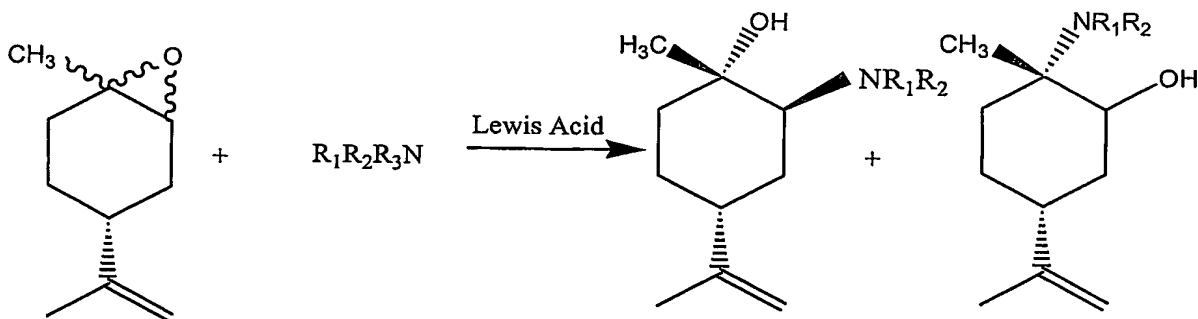
wherein step (b) comprises converting the amine adduct of Formula (2a) to the acid salt of Formula (6a); and

wherein step (c) comprises base hydrolyzing Formula (6a) to form the (+)-p-mentha-2,8-diene-1-ol analog of Formula (5a).

14. The process according to claim 13 wherein the at least one amine is selected from the group consisting of primary amines wherein R_1 is an alkyl or aryl group and R_2 and R_3 are H; secondary amines wherein R_1 and R_2 are alkyl or aryl groups and R_3 is H; and tertiary amines wherein R_1 , R_2 and R_3 are alkyl or aryl groups.

15. The process according to claim 13 wherein the at least one Lewis acid is selected from the group consisting of alkyl metal halides and metal alkyl ethers.

16. The process according to claim 13 wherein R_5X is methyl iodide.
17. The process according to claim 13 wherein the at least one Lewis acid includes at least one ether having the formula MOR wherein M is a metal and R is an alkyl.
18. A process for preparing (+)-p-mentha-2,8-diene-1-ol, the process comprising:

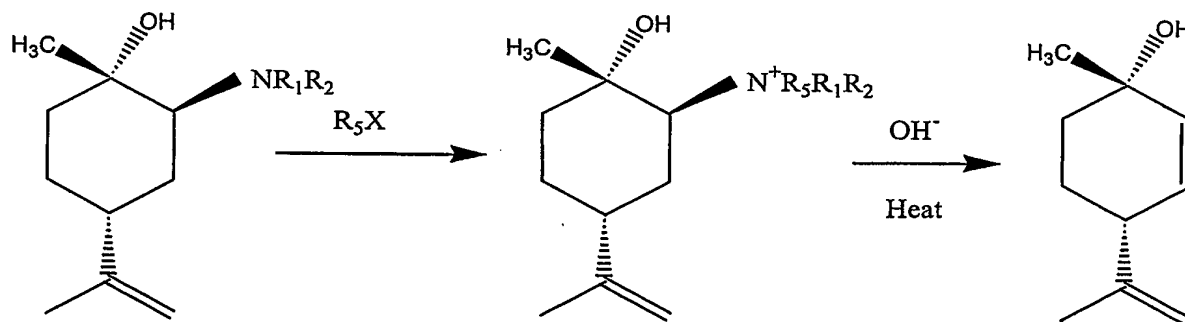


step a

Formula (1b)

Formula (2b)

Formula (3b)



step b

step c

Formula (2b)

Formula (6b)

Formula (5b)

wherein R_1 , R_2 and R_3 are H, alkyl or aryl groups;

wherein R_5 is an H, alkyl or aryl;

wherein X is a halide;

wherein step (a) comprises reacting (+)-limonene oxide having the Formula (1b) with at least one amine of the formula $R_1R_2R_3N$ in the presence of at least one Lewis acid to form amine adducts having the Formula (2b) and Formula (3b);

wherein step (b) comprises converting the amine adduct of Formula (2b) to the acid salt of Formula (6b); and

wherein step (c) comprises base hydrolyzing Formula (6b) to form the (+)-p-mentha-2,8-diene-1-ol of Formula (5b).

19. The process according to claim 18 wherein the at least one amine is selected from the group consisting of primary amines wherein R_1 is an alkyl or aryl group and R_2 and R_3 are H; secondary amines wherein R_1 and R_2 are alkyl or aryl groups and R_3 is H; and tertiary amines wherein R_1 , R_2 and R_3 are alkyl or aryl groups.

20. The process according to claim 18 wherein the at least one Lewis acid is selected from the group consisting of alkyl metal halides and metal alkyl ethers.

21. The process according to claim 18 wherein R_5X is MeI.

22. The process according to claim 18 wherein the at least one Lewis acid includes at least one ether having the formula MOR wherein M is a metal and R is an alkyl.

23. A method for the diastereomeric separation of a mixture of (+)-cis-limonene oxide and (+)-trans-limonene, the method comprising:
reacting the mixture with an amine in the presence of a Lewis acid; and
recovering the (+)-cis-limonene oxide that does not react with the amine.